3)

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-183181
(43)Date of publication of application : 15.07.1997

(51)Int.Cl. B32B 9/00
B32B 7/02
B32B 7/02
B32B 15/01
B32B 15/04
C23C 14/08
G02F 1/1343

(21)Application number : 08-319045
(22)Date of filing : 29.11.1996

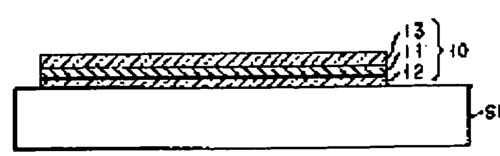
(71)Applicant : TOPPAN PRINTING CO LTD
(72)Inventor : FUKUYOSHI KENZO
KIMURA YUKIHIRO
KOGA OSAMU
IMAYOSHI KOJI
DOCHI KATSUNORI

(30)Priority

| Priority number | Priority date | Priority country |
|---|---|---|
| 07 88797 | 22.03.1995 | JP |
| 07 88798 | 22.03.1995 | JP |
| 07 88799 | 22.03.1995 | JP |
| 07223403 | 31.08.1995 | JP |
| 07223405 | 31.08.1995 | JP |

## (54) FORMING OF MULTI-LAYER CONDUCTIVE FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a conductive film which is thin and displays a favorable conductivity by a method wherein the multi-layer conductive film has a transparent oxide thin film consisting of an indium oxide and the oxide of a metal element which does not have a solid solution region with silver substantially.
SOLUTION: This multi-layer conductive film 10 consists of a silver based thin film 11 which is formed of a silver based metal material, a first transparent oxide thin film 12 which is formed on the first surface of the silver based thin film 11, and a second transparent oxide thin film 13 which is formed on the second surface of the silver based thin film 11. The multi-layer conductive film 10 is formed on a substrate SUB. Both of the first and second transparent oxide thin films 12 and 13 are formed of a mixed oxide which contains a first metal oxide material consisting of an indium oxide, and a



second metal oxide material consisting of the oxide of a metal element which does not have a solid solution region with silver substantially.

LEGAL STATUS

| | |
|---|---|
| [Date of request for examination] | 20.12.1999 |
| [Date of sending the examiner's decision of rejection] | |
| [Kind of final disposal of application other than the examiner's decision of rejection or application converted registration] | |
| [Date of final disposal for application] | |
| [Patent number] | 3191704 |
| [Date of registration] | 25.05.2001 |
| [Number of appeal against examiner's decision of rejection] | |
| [Date of requesting appeal against examiner's decision of rejection] | |
| [Date of extinction of right] | |

* NOTICES *

JPO and NCIPI are not responsible for any
damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The silver system thin film which consists of a silver system metallic material which has the 1st field and this 1st field, and the 2nd field that counters, the 1st transparence oxide thin film formed on the 1st [ of this silver system thin film ] field, and the 2nd transparence oxide thin film formed on the 2nd [ of this silver system thin film ] field -- having -- this -- the 1st and 2nd transparence oxide thin films The 1st metallic-oxide ingredient which consists of an indium oxide independently, respectively, The formation approach of the multilayer electric conduction film characterized by the thing which used the deposition technique for the multilayer electric conduction film currently formed with the mixed oxide containing the 2nd metallic-oxide ingredient which consists of an oxide of a metallic element which does not have a dissolution region with silver substantially, and to form.
[Claim 2] The formation approach of the multilayer electric conduction film according to claim 1 that a deposition technique is a sputtering technique.
[Claim 3] The formation approach of the multilayer electric conduction film according to claim 1 or 2 chosen from the groups which a metallic element without a dissolution region with silver becomes from titanium, a zirconium, a tantalum, niobium, a hafnium, a cerium, a bismuth, germanium, silicon, chromium and those 2, or the combination beyond it.
[Claim 4] The formation approach of claim 1 to which a metallic element without a dissolution region with silver occupies 5 thru/or 50 atom % of sum total atomic weight with an indium element thru/or the multilayer electric conduction film of three given in any 1 term.
[Claim 5] The formation approach of claim 1 whose silver system metallic material is the alloy of a silver element and the different-species element which prevents the migration of a silver element thru/or the multilayer electric conduction film of four given in any 1 term.
[Claim 6] The formation approach of the multilayer electric conduction film according to claim 5 chosen from the groups which a different-species element becomes from aluminum, copper, nickel, cadmium, gold, zinc, magnesium and these 2, or the combination beyond it.
[Claim 7] The formation approach of the multilayer electric conduction film according to claim 5 chosen from the groups which a different-species element becomes from tin, an indium, titanium, a cerium, silicon and these 2, or the combination beyond it.
[Claim 8] The formation approach of claim 1 in which a silver system thin film has 2 thru/or the thickness of 20nm thru/or the multilayer electric conduction film of seven given in any 1 term.
[Claim 9] The formation approach of the multilayer electric conduction film according to claim 7 that a silver system metallic material contains the copper or gold of 0.1 thru/or 3 atom %.
[Claim 10] The formation approach of the multilayer electric conduction film according to claim 8 or 9 that the 1st and 2nd transparence oxide thin films have 2.1 or more high refractive indexes, respectively.
[Claim 11] The formation approach of claim 1 in which a silver system thin film has the thickness of 50nm or more thru/or the multilayer electric conduction film of seven given in any 1 term.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the formation approach of the multilayer electric conduction film of having started the formation approach of the multilayer electric conduction film, especially having excelled in preservation stability.
[0002]
[Description of the Prior Art] The electrode plate with which the transparent electrode film or a reflexibility electrode layer was prepared on substrates, such as glass and a plastic film, is widely used for the I/O electrode which carries out a direct input from the display screen of the electrode for a display of various displays, such as a liquid crystal display, or a display.
[0003] For example, the transparent electrode plate used for a liquid crystal display A glass substrate and the light filter layer which is prepared in the pixel part on this glass substrate, and colors that transmitted light red, green, and blue for every pixel, respectively, The light-shielding film which is prepared in the part between the pixels on the above-mentioned glass substrate (about pixel Mabe), and prevents the light transmission from this pixel Mabe grade, That body is constituted by the protective layer prepared all over the above-mentioned light filter layer, the transparent electrode formed on this protective layer, and the orientation film formed on this transparent electrode. Membranes are formed by sputtering and the transparent electrode is constituted by the transparence electric conduction film etched into the predetermined pattern.
[0004] As this transparence electric conduction film, the ITO thin film which added the tin oxide is widely used into that high conductivity, therefore indium oxide, that specific resistance is 2.4x10-4 ohm-cm about, and, in the case of the 240nm thickness usually applied as a transparent electrode, that sheet resistivity is about 10ohm/**.
[0005] Moreover, although the thin film (Nesa membrane) which added the tin-oxide thin film besides ITO, and added antimony oxide to the tin oxide, the thin film which added the aluminum oxide to the zinc oxide are known, each of these is inferior to the above-mentioned ITO thin film in the conductivity, and since chemical resistance or a water resisting property to an acid, alkali, etc. is inadequate, generally they has not spread.
[0006] By the way, in the above-mentioned display unit or the I/O device, it is required that should ask, the eburnation of above-mentioned transparent electrode PA evening-N should be demanded in connection with this, it should compare, and increasing a pixel consistency and displaying a precise screen in recent years should constitute the terminal area of the above-mentioned transparent electrode from a pitch which is about 100 micrometers of **. Moreover, in the method (COG) with which direct continuation of the IC for liquid crystal actuation is carried out to a substrate in liquid crystal display equipment, the advanced etching processing suitability which wiring may have the part of thin width of face called width of face of 20-50 micrometers, and is not in the former, and high conductivity (low resistivity) are demanded. The above-mentioned ITO ingredient cannot meet such a demand.
[0007] Moreover, on the other hand, enlargement of the display screen is also called for, and in order to form the transparent electrode of a precise pattern which was mentioned above about such a big screen and to enable it to impress sufficient driver voltage for liquid crystal moreover,

it is necessary to use the transparence electric conduction film which has the high conductivity below 5ohms / **, as the above-mentioned transparent electrode. moreover -- in addition, when performing the multi-gradation display of 16 or more gradation in the liquid crystal display of the simple matrix actuation method using STN LCD etc., low sheet resistivity is demanded of the pan below 3ohms / **. The above-mentioned ITO ingredient cannot meet such a demand, either.
[0008] By the way, in a metal, silver is a metal with the highest conductivity, and even if it forms in a thin film, it can secure sufficient transparency and conductivity. For example, in the thickness of 5-30nm, silver indicates the sheet resistivity of about 2-5ohms / ** to be the transparency which fully penetrates the light. Therefore, silver is promising as an electrical conducting material which fills the above-mentioned low resistivity demand.
[0009] However, if silver is left at the room temperature in air, it will receive breakage in about one week. Silver reacts with the sulfur compound and water which exist in air, and a sulfide and an oxide will generate it on the front face, and, more specifically, it will deteriorate on it. Since it is such, silver is not regularly used as the light reflex nature metal electrode of a reflective mold liquid crystal display, or a light reflex plate, although the high screen display of contrast with a reflection factor higher than aluminum is possible again.
[0010] On the other hand, in JP,63-173395,A, JP,1-12663,A, JP,2-37326,A, and the 7thICVM held in Japan in 1982, the transparence multilayer electric conduction film of the three-tiered structure in which the ITO thin film or the indium oxide thin film (IO thin film) was formed at the table rear face of a silver thin film is proposed. The transparence multilayer electric conduction film of this three-tiered structure has sheet resistivity with low about 5ohms / ** extent, and the application to the above-mentioned transparent electrode was expected taking advantage of that high conductivity.
[0011] however, the moisture in the air into which it invaded from the laminating interface etc. in addition also in the electric conduction film of the above-mentioned conventional three-tiered structure when the silver thin film passed for two weeks at the room temperature in air -- combining -- the front face -- an oxide -- generating -- silverfish -- when the defect of a ** was produced, for example, it applied to the transparent electrode of a liquid crystal display, there was a trouble of being easy to make the display screen producing a display defect etc.
[0012]
[Problem(s) to be Solved by the Invention] Therefore, this invention shows good conductivity with a thin film, and, moreover, degradation with the passage of time makes it a technical problem to offer the formation approach of the electric conduction film of having excelled in preservation stability few.
[0013]
[Means for Solving the Problem] The silver system thin film with which the above-mentioned technical problem consists of a silver system metallic material which has the 1st field and this 1st field, and the 2nd field that counters according to this invention, the 1st transparence oxide thin film formed on the 1st [ of this silver system thin film ] field, and the 2nd transparence oxide thin film formed on the 2nd [ of this silver system thin film ] field -- having -- this -- the 1st and 2nd transparence oxide thin films The 1st metallic-oxide ingredient which consists of an indium oxide independently, respectively, It is attained by the formation approach of the multilayer electric conduction film characterized by the thing which used the deposition technique for the multilayer electric conduction film currently formed with the mixed oxide containing the 2nd metallic-oxide ingredient which consists of an oxide of a metallic element which does not have a dissolution region with silver substantially, and to form.
[0014] When examination is repeated wholeheartedly that the transparence multilayer electric conduction film which this invention persons show good conductivity with a thin film, moreover does not have degradation with the passage of time, and was excellent in preservation stability should be developed, as a transparence oxide thin film formed in both sides of a silver system thin film When the mixed oxide of indium oxide and predetermined metallic oxides, such as cerium oxide and titanium oxide, was used instead of the ITO thin film or IO thin film, the multilayer electric conduction film obtained found out having very high stability and moisture resistance. As a result of advancing research further based on this knowledge, by using the

mixed oxide of indium oxide and the oxide of a metallic element which does not have a dissolution region with silver substantially as a transparence oxide thin film formed in both sides of a silver system thin film, this invention persons found out that the desired end could be attained, and decided to form the multilayer electric conduction film concerned using a deposition technique.

[0015]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained to a detail with reference to an attached drawing. Drawing 1 shows the cross section of the multilayer electric conduction film 10 of the three-tiered structure formed on the substrate by the approach of this invention. This multilayer electric conduction film 10 is constituted by the 2nd transparence oxide thin film 13 formed in the 2nd field (front face) of the 1st transparence oxide thin film 12 formed in the 1st field (rear face) of the silver system thin film 11 formed with the silver system metallic material, and the silver system thin film 11, and the silver system thin film 11. The multilayer electric conduction film 10 is formed on Substrate SUB.

[0016] the mixed oxide with which the 1st and 2nd transparence oxide thin films 12 and 13 all contain the 1st metallic-oxide ingredient which consists of indium oxide, and the 2nd metallic-oxide ingredient which consists of oxide of a metallic element which does not have a dissolution region with silver substantially -- formation -- now, it is. In addition, although the 1st and 2nd transparence oxide thin films 12 and 13 do not need to be formed with the same ingredient, forming with the same ingredient is convenient on manufacture of the multilayer electric conduction film 10.

[0017] In this invention, as for the metallic element which does not have a dissolution region with silver substantially, the amount of dissolution with silver means the metallic element below 10 atom % in a room temperature (25 degrees C). As such a metallic element, semimetals, such as lanthanides, such as high-melting transition metals, such as titanium (Ti), a zirconium (Zr), a tantalum (Ta), and niobium (Nb), and a cerium (Ce), a bismuth (Bi), germanium (germanium), and silicon (Si), chromium (Cr), etc. can be illustrated. Even if these metallic elements are independent, they can be used also with the gestalt of two or more combination.

[0018] By applying the mixed oxide which blended with indium oxide the oxide of a metallic element which does not have a dissolution region with silver in both sides of the silver system thin film 11 substantially, although this invention is not restrained by any theory Dissolution-izing with the silver element in the silver system thin film 11 and an indium element and the migration to the inside of both the transparence oxide thin film of a silver element are prevented, and what has and raises the stability with the passage of time and the moisture resistance of the multilayer electric conduction film concerned is believed.

[0019] As for the amount of the 2nd metallic-oxide ingredient, it is desirable that the metallic element which does not have substantially the metallic element part, i.e., a dissolution region with silver, is the amount which accounts for 5% or more of rate of sum total atomic weight with the indium element part of the 1st metallic-oxide ingredient. The addition effectiveness of the 2nd metallic-oxide ingredient is that the amount of a metallic element which does not have a dissolution region with silver substantially is under pentatomic % in the inclination which is not enough. As for the amount of a metallic element which does not have a dissolution region with silver substantially, it is still more desirable that it is more than 10 atom % of sum total atomic weight with an indium.

[0020] On the other hand, as for the amount of the 2nd metallic oxide, it is desirable that the metallic element which does not have substantially the metallic element part, i.e., a dissolution region with silver, is the amount which accounts for 50% or less of rate of the sum total of atomic weight with the indium element part of the 1st metallic oxide. If the amount of a metallic element which does not have a dissolution region with silver substantially exceeds 50 atom %, as for the oxide thin film obtained, adhesion with a silver system thin film will tend to fall. Moreover, when such a lot of elements exist, it becomes difficult, and it becomes empty and a crack and the inclination for a membrane formation rate to fall have processing of the target used for the membrane formation explained in full detail henceforth. As for the amount of a metallic element which does not have a dissolution region with silver substantially, it is still more desirable that it

is below 40 atom % of sum total atomic weight with an indium, and it is most desirable that it is below 30 atom %.
[0021] As for the 1st and 2nd transparence oxide thin films 12 and 13, it is all desirable to have 30 thru/or the thickness of 100nm. If the thickness exceeds 100nm, the reflected light in the front face of the oxide thin film and the reflected light in silver system thin film 11 front face will interfere, and a color will be produced.
[0022] Although the silver system thin film 11 may be formed by the silver independent, in order to prevent silver migration, it is desirable to contain different-species elements other than the silver which prevents silver migration. When the example of such a different-species element is given, they are aluminum (aluminum), copper (Cu), nickel (nickel), cadmium (Cd), gold (Au), zinc (Zn), magnesium (Mg), tin (Sn), an indium (In), titanium (Ti), a zirconium (Zr), a cerium (Ce), silicon (Si), lead (Pb), and palladium (Pd). Aluminum, copper, nickel, cadmium, gold, zinc, and magnesium also have the effectiveness of raising conductivity, among these elements, and tin, an indium, titanium, a zirconium, a cerium, and silicon also have the effectiveness of raising adhesion with the oxide thin films 12 and 13. Especially since it contributes also to stabilization of the silver system thin film 11, gold is desirable.
[0023] As for such a different-species element, it is desirable to be contained in the silver system thin film 11 at a rate of 0.1 thru/or 3 atom %. When the amount is under 0.1 atom %, and the silver migration prevention effectiveness is not fully demonstrated but exceeds another side 3 atom %, it is in the inclination for the conductivity of the silver system thin film 11 to fall. Especially gold is in the inclination to leave an etch residue in the case of etching, when 3 atom % is exceeded. As for gold, it is desirable to be contained at a rate below 2.5 atom %.
[0024] In order to secure the conductivity which may be satisfied, as for the silver system thin film 11, it is desirable to have the thickness of 2nm or more. In addition, the thickness of this silver system thin film 11 differs by whether the multilayer electric conduction film 10 is used as a transparent electrode, or it is used as a light reflex nature electrode.
[0025] A glass substrate (refractive index n= 1.5) is used for drawing 5 and drawing 6 as a substrate SUB. The multilayer electric conduction film 10 of the structure which moreover pinched the silver thin film 11 with the refractive index n= 2.3 with the 1st and 2nd transparence oxide thin films 12 and 13 of 40nm of thickness, respectively is formed. It is what shows change of the reflection factor R of the multilayer electric conduction film at the time of changing the thickness of the silver thin film 11, and permeability T. Drawing 5 The result at the time of setting thickness of the silver thin film 12 to 10nm (curve a), 15nm (curve b), 20nm (curve c), and 50nm (curve d) drawing 6 The result at the time of setting thickness of the silver thin film 11 to 50nm (curve d), 75nm (curve e), 100nm (curve f), and 200nm (curve g) is shown. In drawing 5 and drawing 6 , the notation T in the parenthesis next to the sign which shows each curve shows permeability, and Notation R shows a reflection factor.
[0026] The spectral characteristic of the transparency subject whom the multilayer electric conduction film shows about 80% or more of permeability that the thickness of the silver thin film 11 is to 20nm is shown so that drawing 5 may show. Moreover, when the thickness of the silver thin film 11 is set to 50nm or more so that drawing 6 may show, the multilayer electric conduction film comes to show the spectral characteristic of the reflective subject who shows about 80% or more of reflection factors. If especially the thickness of a silver thin film is set to 75nm or more, the reflection factor of the multilayer electric conduction film is saturated mostly, permeability will be set to about 0 and a reflection factor will completely be saturated with 200nm.
[0027] It returns to drawing 1 and the multilayer electric conduction film 10 of this invention is formed on the suitable substrate SUB using deposition techniques, such as vacuum deposition, sputtering, and ion plating.
[0028] As for especially the transparence oxide thin films 12 and 13, producing with a sputtering technique is desirable, and in case the transparence oxide thin film concerned is formed especially, when the silver system thin film 11 exists, it is still more desirable to produce with DC-sputtering techniques, such as DC sputtering and an RF-DC sputtering technique. If RF sputtering is used, Substrate SUB is heated and the migration of the silver in the silver system

thin film 11 arises, and the silver system thin film 11 not only deforms spherically, but the oxygen plasma will occur and it will be similarly accompanied by silver migration and spherical deformation of the silver system thin film as the result.
[0029] the temperature lowest possible when the silver system thin film 11 exists, in order that the temperature of Substrate SUB may prevent the migration of the silver in the silver system thin film concerned -- 180 degrees C or less are more preferably set as the temperature around 120 degrees C. This temperature may be a room temperature.
[0030] As for the inside of a sputtering system, it is desirable that moisture does not exist, in order to prevent the migration of the silver in the silver system thin film 11. Now, Substrate SUB is purified before forming the multilayer electric conduction film 10 on Substrate SUB. According to the class of ingredient of Substrate SUB, ion bombardment, reverse sputtering, ashing, ultraviolet-rays washing, glow discharge processing, etc. can perform this clarification.
[0031] The target used in order to form the transparence oxide thin films 12 and 13 with a sputtering technique etc. The 1st metallic-oxide ingredient, i.e., powder of an indium oxide and powder of the 2nd metallic-oxide ingredient, A binder like paraffin, a dispersant, and a solvent (usually water) are suitably added to mixture with the powder of the oxide of a metallic element which does not have a dissolution region with silver substantially. Namely, in grinding / mixing equipments, such as a ball mill 10 - 40-hour mixing and grinding of are usually done until oxide powder comes to have the mean particle diameter of 2 micrometers or less preferably. It is the obtained detailed powder mixture preferably 50-200kg/cm2 Press forming is carried out under a pressure and it calcinates under an oxygen ambient atmosphere. Unnecessary components, such as a binder and a dispersant, are removed by this baking, and a precise sintered compact is obtained. In order to obtain a precise sintered compact, the temperature of burning temperature of 1000 degrees C or more is desirable. They are 1200 degrees C or more and 1800 degrees C or less in temperature more preferably. When burning temperature exceeds 1800 degrees C, the 2nd metallic oxide fuses, and a non-wanted reaction is triggered and it is in the inclination with the silver system thin film 11 to reduce the conductivity of the multilayer electric conduction film, and the light transmission nature of a transparence oxide thin film.
[0032] In this way, when the configuration is unsuitable, grinding of the obtained target can be carried out with a grinder, or it can be orthopedically operated by cutting by a diamond cutter etc. The presentation of a target is made the same as the presentation of the desired transparence oxide thin films 12 and 13. That is, the transparence oxide thin film of the same presentation as the presentation of a target is obtained. In addition, in order to adjust the conductivity of a target, a consistency, reinforcement, etc., small quantity, in addition ** are good in the oxide of elements, such as tin, magnesium, zinc, a gallium, aluminum, silicon, germanium, antimony, a bismuth, and titanium. Although these additives may be introduced into the transparence oxide thin film 12 formed and 13, it is desirable to add at a target at a little quantitative rate which does not have an adverse effect on them.
[0033] The silver system thin film 11 has a large membrane formation rate, and since it is the same as the transparence oxide thin films 12 and 13, it is desirable to produce continuously with the transparence oxide thin films 12 and 13 with the same equipment with the reason which can form membranes, and a DC-sputtering technique.
[0034] The target used in order to produce the silver system thin film 11 by sputtering is a target containing the target which consists only of silver or silver, and the different-species element which prevents silver migration. Although the target containing silver and a different-species element is in the gestalt of the alloy of silver and a different-species element preferably, it may be in the gestalt which embedded the chip of a different-species element to silver. The presentation of a target is the same as the presentation of the desired silver system thin film 11.

[0035] After carrying out sequential formation of the 1st transparence oxide thin film 12, the silver system thin film 11, and the 2nd transparence oxide thin film 13 on Substrate SUB under the above-mentioned monograph affair, it is desirable to present annealing processing with this multilayer at the temperature of 200 degrees C or more. The conductivity of a multilayer improves further by this annealing processing.

[0036] Each can carry out patterning of the transparence oxide thin films 12 and 13 and the silver system thin film 11 preferably by etching processing by the nitric-acid system etching reagent. That is, after forming the multilayer electric conduction film 10 concerning this invention on Substrate SUB, on the transparence oxide thin film 13 of the maximum upper layer, the resist usually used is applied and this resist film is formed in the shape of [ desired ] a pattern for example, at an electrode pattern configuration. By etching the part exposed from this resist pattern with a nitric-acid system etching reagent, it is possible to carry out patterning to the pattern configuration in which the thin film of the three above-mentioned layers carried out location adjustment mutually.
[0037] As this etching reagent, although a nitric acid can also be used independently, the mixed acid which comes to add other acids, such as a hydrochloric acid, a sulfuric acid, and an acetic acid, to a nitric acid may be used. As for an etching reagent, it is desirable that it is the mixed acid of a sulfuric acid and a nitric acid. A sulfuric acid dissolves a transparence oxide thin film preferentially, and a nitric acid dissolves a silver system thin film preferentially. As for sulfuric-acid concentration, in the case of the mixed acid of this sulfuric acid and nitric acid, it is desirable that it is higher than nitric-acid concentration. Thereby, although the side etch rate of a transparence oxide thin film and a silver system thin film is different, the amount of side etching of these thin films can be made in agreement, and the pattern configuration of these thin films can be adjusted. Preferably, the weight ratio 100:0.05 of a sulfuric acid and a nitric acid thru/or the mixed acid of 100:50 can be used. In an etching reagent, oxidizers, such as chlorides, such as nitrates, such as sulfates, such as an ammonium sulfate, a peroxy ammonium sulfate, and potassium sulfate, an ammonium nitrate, and cerium-nitrate ammonium, a sodium chloride, and potassium chloride, chrome oxide, cerium oxide, and a hydrogen peroxide, other acetic acids, a selenic acid, a phosphoric acid, alcohol, a surfactant, etc. can be added suitably. The temperature of 30 degrees C can perform etching in 40 - 60 seconds. By this etching processing, it has side etching width of face of about 0-4 micrometers, and a pattern configuration cannot be confused and the electrode pattern which has the minimum width of face 20 thru/or the 50-micrometer thin line section can be formed.
[0038] Thus, when the multilayer electric conduction film is etched, in order to protect the etched side edge side from degradation by moisture, it is desirable to form a dampproof transparence thin film. Drawing 2 shows the multilayer electric conduction film 10 of this invention in the gestalt protected with the dampproof transparence thin film 21 of electric insulation. In drawing 2 , each multilayer electric conduction film 10 formed on Substrate SUB is formed in the shape of [ which is prolonged by the above-mentioned etching in the direction which intersects perpendicularly with the space of drawing, respectively ] a stripe, and the whole including the etched side face is covered with the dampproof transparence thin film 21.
[0039] As for the dampproof transparence thin film 21, it is desirable that dampproofing forms with the oxide of metals, such as silicon, titanium, a zirconium, and a tantalum, because it is high. Especially as such a metallic oxide, the oxide of silicon is desirable.
[0040] The dampproof transparence thin film 21 is sum total thickness with the transparence oxide thin film 13, and it is desirable that it is 20nm or more. In addition, the dampproof transparence thin film 21 is sum total thickness with the transparence oxide thin film 13, and it is desirable that it is 100nm or less. If this total thickness exceeds 100nm, the reflected light on the front face of a protective coat concerned and the reflected light in the silver system thin film 11 will interfere and color. The dampproof transparence thin film 21 is usually formed by the thickness of 20nm - 70nm. The dampproof transparence thin film 21 can be formed with the membrane formation technique of the transparence oxide thin films 12 and 13, and the same technique. In addition, when the dampproof transparence thin film 21 is formed, annealing treatment for the conductive improvement described above is performed after forming this thin film 21.
[0041] The multilayer electric conduction film formed of this invention can be used as the transparent electrode of various liquid crystal displays, or a light reflex nature electrode. In addition, when the multilayer electric conduction film 10 is transparent, while the basic structure of a transparent electrode plate is shown that drawing 1 explains drawing 3 R> 3 and drawing 4

henceforth transparently [ Substrate SUB ], as drawing 4 is explained henceforth, when the multilayer electric conduction film 10 is light reflex nature, the basic structure of a light reflex nature electrode plate is also shown.
[0042] Drawing 3 is the outline sectional view showing an example of a transparency mold liquid crystal display. The transparency mold liquid crystal display 30 shown in drawing 3 has the transparence substrates 31 and 41 of the couple by which opposite arrangement was carried out by having predetermined spacing with Spacer SP. The transparence substrate 31 is located in an observer side, and the transparence substrate 41 is located in the tooth-back side. a group which is prepared to a pixel part on the field which meets the transparence substrate 41 of the observer side transparence substrate 31, and colors the transmitted light red, green, and blue for every pixel -- the light filter layer 32 which consists of light filter CF1 -CFn (these may be named generically and it may be hereafter called a light filter CF) is formed, and the protective layer 33 is formed on it. Usually, the light-shielding film (not shown) which prevents transparency of the light from this part is formed in pixel Mabe between pixels. On a protective layer 33, the transparent electrode (only one transparent electrode appears in drawing 3 ) 34 of the shape of two or more stripe formed with predetermined spacing is formed, and the orientation film 35 is formed on it. The IC chip CP for liquid crystal actuation is formed in the part which extends on the transparence substrate 31 from the liquid crystal cell of a transparent electrode 34.
[0043] The polarization film 36 is formed in another field of the transparence substrate 31. On the field which meets the transparence substrate 31 of the tooth-back side transparence substrate 41, it has respectively fixed spacing, 421-42n (hereafter, these may be named generically and it may be called a transparent electrode 42) of transparent electrodes which extend in the extension direction of a transparent electrode 34 and the direction which intersects perpendicularly is formed, and the orientation film 43 is formed on it.
[0044] The polarization film 44 is formed in another field of the transparence substrate 41. The transparence substrates 31 and 41 are formed with a light transmission nature ingredient. As such an ingredient, a glass plate, a plastics board, and a plastic film (what contains a polarization film, a phase contrast film, and a lens sheet, and has the rebound ace court layer which consists of GASUPARI, a - layer, or hard synthetic resin is included) can be illustrated.
[0045] And the liquid crystal ingredient LC is enclosed with the tooth space between the transparence substrates 31 and 41. any of the thing of the type with which these liquid crystal, such as a nematic liquid crystal, a ferroelectric liquid crystal, half-ferromagnetism liquid crystal, cholesteric liquid crystal, a smectic liquid crystal, and HOMEOTORO pick liquid crystal, was distributed in the polymeric material as a liquid crystal ingredient LC according to the actuation mode -- although -- it can be used. Moreover, the actuation modes of a liquid crystal display may be the Twisted Nematic (TN) mode, super-twisted-nematic (STN) mode, the rate (ECB) mode of an electric-field control birefringence, the rate Twisted Nematic (BTN) mode of a birefringence, optical compensation bend (OCB) mode, guest host mode, etc. In addition, as for liquid crystal, at the time of light transmission (at the time [ The case of Nor Marie White's TN, and STN ] of electrical-potential-difference OFF), it is desirable to have a refractive index (for example, 1.5 thru/or 1.6) near the refractive index (usually about 1.5) of a transparence substrate. It is because the inside of the liquid crystal layer LC can be penetrated without the light which advanced into it refracting and reflecting if a liquid crystal ingredient has such a refractive index.
[0046] Drawing 4 is the outline sectional view showing an example of a reflective mold liquid crystal display. The transparency mold liquid crystal display 50 shown in drawing 4 has the substrates 51 and 61 of the couple by which opposite arrangement was carried out by having predetermined spacing with Spacer SP. A substrate 51 is located in an observer side and is transparent. A substrate 51 may be located in the tooth-back side, and may be transparent, or may be opaque.
[0047] On the field which meets the substrate 61 of the observer side transparence substrate 51, 531-53n (hereafter, these may be named generically and it may be called a transparent electrode 53) of transparent electrodes of the shape of a stripe formed with predetermined spacing through the light-scattering film 52 is formed, and the orientation film 54 is formed on it.

[0048] The polarization film 55 is formed in another field of the transparence substrate 51, and the light-scattering film 56 is formed on it. The transparence substrate 51 can be formed with the same ingredient as the transparence substrates 31 and 41 in the liquid crystal display shown in drawing 3 .
[0049] On the field which meets the transparence substrate 51 of the tooth-back side substrate 61, it has predetermined spacing, two or more stripe-like light reflex nature electrodes (only one reflexibility electrode appears in drawing 4 ) 62 which extend in the extension direction of a transparent electrode 53 and the direction which intersects perpendicularly are formed, and the orientation film 63 is formed on it. The IC chip CP for liquid crystal actuation is formed in the part which extends on a substrate 61 from the liquid crystal cell of the light reflex nature electrode 62.
[0050] The tooth-back side substrate 61 can be formed with the same ingredient as the transparence substrates 31 and 41 in the liquid crystal display 30 shown in drawing 1 , when transparent, but since it reduces regular-reflection light, it is desirable to perform concavo-convex processing to the front face of the ingredient concerned, or to form a light-scattering layer in it, and to make it opaque. It can form with the ingredient which made synthetic resin (it usually has the refractive index of 1.3 thru/or 1.7) distribute the transparence powder which has this and a different refractive index as a light-scattering layer. Mean particle diameter is below the wavelength of light, and transparence powder can illustrate inorganic powder, such as titanium oxide besides granularity resin powder (for example, microcapsule of a fluororesin), a zirconium dioxide, lead oxide, an aluminum oxide, silicon oxide, a magnesium oxide, a zinc oxide, a thorium oxide, cerium oxide, a calcium fluoride, and magnesium fluoride. As transparence powder, cerium oxide, a calcium fluoride, and magnesium fluoride are desirable.
[0051] The same liquid crystal ingredient LC as what was explained about the transparency mold liquid crystal display 30 is enclosed with the tooth space between substrates 51 and 61. The actuation mode of a liquid crystal display may be each mode, such as TN, STN, BTN, OCB, and a guest host. Similarly, as for liquid crystal, at the time of light transmission (at the time [ Nor Marie White's TN, and the case of STN LCD ] of electrical-potential-difference OFF), it is desirable to have a refractive index (for example, 1.5 thru/or 1.6) near the refractive index (usually about 1.5) of a transparence substrate. It is because the inside of the liquid crystal layer LC can be penetrated without the light which advanced into it refracting and reflecting if a liquid crystal ingredient has such a refractive index.
[0052] Now, the multilayer electric conduction film 10 of this invention can be used as transparent electrodes 34 and 42 and/or 53 also in any of the liquid crystal display of drawing 3 and drawing 4 , even if it is in any of the gestalt protected by the protective coat 21 shown in drawing 2 , or the gestalt which is not protected. In that case, since the multilayer electric conduction film 10 needs the transparent thing, as stated above, it is desirable [ the film / the silver system thin film 11 ] to have the thickness of 20nm or less.
[0053] Moreover, generally, since the refractive index of a light filter CF and the transparence substrates 31, 41, and 51 is about 1.5 and the refractive indexes of the liquid crystal ingredient LC are 1.5 thru/or 1.6, in order for the refractive index of the multilayer electric conduction film 10 to reduce a reflection factor as a thing near those refractive indexes and to increase permeability, it is much more desirable [ especially the thickness of the silver system thin film 11 ] to be referred to as 4 thru/or 17nm 17nm or less.
[0054] Although drawing 7 is the same configuration as the multilayer electric conduction film explained about drawing 5 The refractive index of the transparence oxide thin films 12 and 13 is set to 2.3. The thickness of the 1st transparence oxide thin film 12 35nm, When the refractive index of 40nm and liquid crystal is set to 1.5 for the thickness of the polyimide orientation film formed 37nm and on it in the thickness of the 2nd transparence oxide thin film 13, The result of having simulated the permeability (T) and reflection factor (R) of the multilayer electric conduction film at the time of changing the thickness of the silver system thin film 11 with 9nm (curve a), 11nm (curve b), 13nm (curve c), 15nm (curve d), and 17nm (curve e) is shown. In drawing, the notation T in the parenthesis attached to the sign which displays a curve expresses permeability, and Notation R expresses a reflection factor. Although a reflection factor is low, if

the thickness of a silver system thin film is [ permeability ] 90% or more in 17nm or less, and the thickness of a silver system thin film exceeds 17nm corresponding to it, permeability with a wavelength [ of light ] of 550nm will tend to be less than 90%, so that drawing 7 may show. In addition, since the thickness of a silver system thin film becomes being less than 4nm with the shape of an island at the time of the membrane formation, it is not desirable.
[0055] In addition, as for the silver system thin film 11, it is desirable to be formed with the copper of silver, 0.1, or 3 atom % or an alloy with gold. If copper or gold is added at such a rate, short wave Nagamitsu's permeability will increase.
[0056] Drawing 8 forms the 40nm [ of each thickness ] copper addition silver thin film (AgCu0.1) of 0.1 atom %, the copper addition silver thin film (AgCu3) of 3 atom %, and a silver thin film on the Xtal substrate with a thickness of 1mm, and shows the result of having measured the spectral transmittance (T). If the copper of 0.1 - 3 atom % is added to silver as shown in this drawing, less than 400nm short wave Nagamitsu's permeability will increase intentionally compared with the case of only silver.
[0057] Drawing 9 shows the sheet resistivity of the various silver system thin films which added copper to silver comparatively (atomic %), and were produced. When a copper addition is three atoms %, the sheet resistivity of the silver-copper alloy of 10nm of thickness is about 5ohm/**, the sheet resistivity of the silver-copper alloy of 15nm of thickness is about 3ohm/**, and, in the case of a copper content of this amount, conductivity is enough [ that sheet resistivity increases as are shown in this drawing and a copper addition increases, but ].
[0058] In addition, also when gold is used instead of copper, the same result as what is shown in drawing 8 and drawing 9 is obtained. Moreover, in order to increase the permeability of short wave Nagamitsu and long wavelength light, as for the transparence oxide thin films 12 and 13, it is desirable to have 2.1 or more refractive indexes. In order to have such a high refractive index, it is desirable to use the oxide of a cerium, titanium, a zirconium, a hafnium, and/or a tantalum as 2nd metallic-oxide ingredient which constitutes a transparence oxide thin film. Especially as such 2nd metallic-oxide ingredient, the oxide of a cerium and titanium is desirable. If an example is given, the refractive index of the transparence oxide thin film which contains a cerium at a rate of 20 atoms %, 30 atoms %, and 40 atom %, respectively will be set to 2.17, 2.24, and 2.30, respectively. In addition, if the metal atom of the 2nd metallic-oxide ingredient is contained more than 10 atom %, while becoming an amorphous Mr. gestalt and being able to carry out patterning with a good precision, that a transparence oxide thin film is amorphous or since it becomes isotropy optically, it can maintain plane of polarization.
[0059] Drawing 10 shows the calculated relation between the refractive index of the transparence oxide thin film of the multilayer electric conduction film of this invention at the time of assuming that the multilayer electric conduction film of this invention contacts a liquid crystal ingredient (a refractive index 1.5 and assumption) through the polyimide orientation film of 40nm of thickness, light transmittance, and a reflection factor. In this case, the thickness of a transparence oxide thin film was optimized. As for Curve b, in drawing 10 , Curve c shows [ Curve a / Curve d ] the case where the refractive index of Curve e is 2.4 about the case where a refractive index is 2.3 about the case where a refractive index is 2.2 about the case where a refractive index is 2.1 about the case where a refractive index is 2.0. In drawing 10 , the notation T in the parenthesis next to the sign which shows each curve shows permeability, and Notation R shows a reflection factor. Permeability improves that the refractive index of a transparence oxide thin film is 2.1 or more, and a reflection factor also falls so that drawing 10 may show.
[0060] When using as a reflexibility electrode 62 of the reflective mold liquid crystal display which shows the multilayer electric conduction film 10 of this invention to drawing 4 , in order to show good light reflex nature, as stated also above, it is desirable [ the multilayer electric conduction film 10 ] to have the silver system thin film 11 which has the thickness of 50nm or more. And as drawing 6 was explained, as for the silver system thin film 11, it is desirable to have the thickness of 200nm or less. Other matters are as having explained drawing 1 , drawing 2 , and drawing 4 .
[0061] As mentioned above, although the multilayer electric conduction film of this invention was

explained mainly about application to a liquid crystal display, the multilayer electric conduction film of this invention can be used as the transparent electrode and light reflex electrode of a solar battery.
[0062]
[Example] Hereafter, an example explains this invention still more concretely.
In example 1 this example, the transparent electrode plate which has the multilayer electric conduction film of this invention was produced.
[0063] This transparent electrode plate was a thing equipped with the transparence multilayer electric conduction film 10 which consists of a transparence oxide thin film 12 with a thickness of 35nm by which has the structure shown in drawing 1 and the laminating was carried out one by one on 0.7mm glass substrate SUB in thickness, and the silver thin film 11 with a thickness of 14nm and the transparence oxide thin film 13 with a thickness of 35nm.
[0064] The transparence oxide thin films 12 and 13 are formed by each with the mixed oxide of titanium oxide ($TiO_2$) and indium oxide ($In_2O_3$), and the content of titanium oxide is an amount from which the Chita atom becomes 20 atom % of an indium atom by metallic element conversion (an oxygen atom is not counted).
[0065] This transparence multilayer electric conduction film formed membranes by the following approaches.
The <preparation of target for transparence oxide thin film formation> mean diameter added a small amount of paraffin as a binder into the mixture of the predetermined rate of the indium oxide powder and titanium oxide powder which are about 2 micrometers, respectively, and did 24-hour grinding and mixing of with the wet ball mill.
[0066] Subsequently, it dried and moisture was removed, after filling up predetermined metal mold with this mixed powder and fabricating it in a predetermined configuration. This Plastic solid is put into an electric furnace, and it calcinates at 1550 degrees C under an oxygen ambient atmosphere for 10 hours, and the Plastic solid was made to sinter while removing paraffin. Grinding of this sintered compact was carried out with the surface grinder, it operated orthopedically with the diamond cutter, and the desired target was obtained.
Vacuum melting of the <preparation of target for silver thin film formation> silver was carried out all over the fusion furnace, casting was carried out into the metal mold by which water cooling was carried out, and it cooled for 3 hours. Grinding of the front face of the acquired casting object was carried out with the surface grinder, the end face was operated orthopedically, and the desired target was obtained.
Sequential washing of the front face of a <washing of glass substrate> glass substrate was carried out with an alkali system surfactant and water. This was held in the vacuum tub of DC magnetron sputtering system, plasma treatment called reverse sputtering was performed, and it washed further.
Without taking out a <production of multilayer electric conduction film> glass substrate out of a vacuum tub, where this glass substrate is maintained to a room temperature, subsequently sequential membrane formation of the transparence oxide thin film 13 was first carried out [ the transparence oxide thin film 12 ] for the silver thin film 11 using the above-mentioned silver target using the above-mentioned transparence oxide target by the sputtering method, using the above-mentioned transparence oxide target again.
[0067] Next, the resist film of an electrode configuration was formed on the transparence oxide thin film 13, and where it etched the part exposed from this resist film for about 40 seconds at 30 degrees C with the mixed-acid etching reagent containing 60.4 % of the weight of sulfuric acids, and 3 % of the weight of nitric acids and location adjustment of the thin film of the three above-mentioned layers is carried out mutually, patterning was carried out to the electrode configuration. Then, annealing treatment of 1 hour was performed to this at 220 degrees C, and the transparence multilayer electric conduction film was formed.
[0068] In this way, the sheet resistivity of the obtained transparence multilayer electric conduction film was about 2.7ohm/**. Moreover, the light permeability is shown in the following table 1. For a comparison, the light permeability is combined about the transparence multilayer electric conduction film of the three-tiered structure which applied IO thin film instead of the

above-mentioned transparence oxide thin films 12 and 13, and it is shown in a table 1.
[0069] Change of an appearance was not observed at all on the front face of ** and the transparence multilayer electric conduction film 10 as having left the transparent electrode plate of an example 1 for eight weeks, and having observed it in air. On the other hand, in the transparence multilayer electric conduction film of the three-tiered structure which applied IO instead of the above-mentioned transparence oxide thin film, much silverfish occurred in two weeks after preservation.
[0070] As mentioned above, while the transparence multilayer electric conduction film concerning this example has the high visible-ray permeability by the side of long wavelength as compared with the conventional example and having uniform and high light transmission in all visible regions, it has very high conductivity, and it has checked excelling in moisture resistance moreover.
[0071] In example 2 this example, the transparent electrode plate was produced like the example 1 except having formed the transparence oxide thin films 12 and 13 with the mixed oxide of titanium oxide ($TiO_2$), cerium oxide ($CeO_2$), and indium oxide. It is metallic element conversion (an oxygen atom is not counted), the content of titanium oxide is an amount from which a titanium atom becomes 16 atom % of an indium atom, and the content of cerium oxide is an amount from which a cerium atom becomes 4 atom % of an indium atom.
[0072] The sheet resistivity of the obtained transparence multilayer electric conduction film 10 was about 2.7ohm/**. The light permeability is combined and shown in a table 1. When this transparent electrode plate was left for eight weeks and observed in air, change of an appearance was not observed at all on the front face of the transparence multilayer electric conduction film like the example 1.
[0073]
[A table 1]
表 1 可視光の透過率（%）

| | 波長 | | | | | |
|---|---|---|---|---|---|---|
| | 450nm | 500nm | 550nm | 600nm | 650nm | 700nm |
| 実施例1 | 95.4 | 97.5 | 95.8 | 93.0 | 89.5 | 81.0 |
| 実施例2 | 95.3 | 97.4 | 95.5 | 93.1 | 89.7 | 81.4 |
| 比較例 | 96.2 | 97.0 | 95.1 | 90.4 | 82.9 | 73.7 |

[0074] Both thickness was set to 39nm, without changing the presentation of the example 3 transparence oxide thin films 12 and 13, except having formed the silver system thin film 11 in 14nm in thickness with the silver-copper alloy which does 0.4 atom % content of copper, the transparence multilayer electric conduction film was formed on the substrate like the example 1, and annealing treatment was performed at 270 degrees C for 1 hour. In this way, the sheet resistivity of the obtained transparence multilayer electric conduction film was about 2.8ohm/**. Moreover, the light permeability is shown in the following table 2.
[0075]
[A table 2]
表 2 可視光の透過率（%）

| | 波長 | | | | | | |
|---|---|---|---|---|---|---|---|
| | 400nm | 450nm | 500nm | 550nm | 600nm | 650nm | 700nm |
| 実施例3 | 81.9 | 93.9 | 97.0 | 97.5 | 95.6 | 92.6 | 85.8 |

[0076] As mentioned above, while the transparence multilayer electric conduction film concerning an example 3 has the high visible-ray permeability by the side of short wavelength

and having uniform light transmission in all visible regions, it has very high conductivity, and moreover, it has checked excelling in moisture resistance.
[0077] In example 4 this example, the transparent electrode plate which has the multilayer electric conduction film of this invention was produced. This transparent electrode plate has the structure shown in drawing 1 , and is equipped with the transparence multilayer electric conduction film 10 which consists of a transparence oxide thin film 12 with a thickness of 39nm by which the laminating was carried out one by one on glass substrate SUB with a thickness of 0.7mm, and the silver alloy thin film 11 with a thickness of 10nm and the transparence oxide thin film 13 with a thickness of 39nm.
[0078] The transparence oxide thin films 12 and 13 are amounts from which each is formed with the mixed oxide of titanium oxide (TiO2), cerium oxide (CeO2), and indium oxide, and it is (not counting an oxygen atom) in metallic element conversion, and it is the amount from which, as for the content of titanium oxide, a titanium atom becomes 19 atom % of an indium atom, and, as for the content of cerium oxide, a cerium atom becomes 1 atom % of an indium atom. Moreover, the silver alloy silver system thin film 11 formed copper with the silver-copper alloy of which 0.3 atom % content is done.
[0079] The sheet resistivity after forming this transparence multilayer electric conduction film 10 by the approach of an example 1 and resemblance and performing annealing treatment of 1 hour at 270 degrees C was about 4.6ohm/**. Moreover, when the visible-ray permeability was measured, it continued throughout the visible region with a wavelength of 400-700nm, 90% or more of high light transmittance was shown, and it has checked that the light transmittance was increasing remarkably in the both sides by the side of the short wavelength of 500nm or less, and the long wavelength of 550nm or more compared with the case where especially the thin film of a silver simple substance is used.
[0080] In example 5 this example, the transparent electrode plate which has the multilayer electric conduction film of this invention was produced. This transparent electrode plate had the structure shown in drawing 1 , and is equipped with the transparence multilayer electric conduction film 10 which consists of the transparence oxide thin film 12 with a thickness of 33nm by which the laminating was carried out one by one on glass **** SUB with a thickness of 0.7mm, a silver system thin film 11 with a thickness of 15nm, and a transparence oxide thin film 13 with a thickness of 34nm.
[0081] The transparence oxide thin films 12 and 13 are all metallic element conversions (an oxygen atom is not counted), and were used as the mixed oxide which added cerium oxide to indium oxide at a rate that a cerium atom becomes 30 atom % of an indium atom. Moreover, the silver system thin film 11 formed gold with the silver-gold alloy of which 1.0 atom % content is done.
[0082] This transparence multilayer electric conduction film was produced by the approach of an example 1 and resemblance, and performed 220 degrees C and annealing treatment of 1 hour. In this way, the sheet resistivity of the obtained transparence multilayer electric conduction film 10 was about 2.9ohm/**. Moreover, the light permeability is shown in drawing 11 .
[0083] Although surface observation was carried out after holding this transparence multilayer electric conduction film 10 that carried out pattern formation under 60 degrees C and conditions of 95% of relative humidity for 500 hours, it was not what produces appearance change at all. In addition, it was 2.24 when the refractive index of the transparence multilayer electric conduction film by this mixed oxide was measured.
[0084] The transparence multilayer electric conduction film 10 of the structure shown in drawing 1 by example 6 example 5, this configuration, and this process was formed on glass substrate SUB. However, although the thickness of the silver system thin film 11 is the same as 15nm, the rate of the gold in the silver-gold alloy which constitutes the silver system thin film 11 was changed to 0.1 to 4 atoms %. The sheet resistivity value of each transparence multilayer electric conduction film and the light transmittance in 610nm are shown in a table 3. In addition, a sheet resistivity value and light transmittance are the values measured after the annealing treatment of 1 hour at 220 degrees C.
[0085]

[A table 3]

| | 金の添加量（原子%） | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0.1 | 0.2 | 0.4 | 0.8 | 1.5 | 2.5 | 4.0 | 0 |
| 面積抵抗 (Ω/□) | 2.81 | 2.83 | 2.82 | 2.85 | 3.28 | 4.13 | 4.94 | 2.81 |
| 光透過率(%) (610nm) | 93.0 | 92.8 | 92.5 | 92.5 | 92.4 | 90.7 | 89.2 | 92.6 |

[0086] Also in the transparence multilayer electric conduction film which has the silver system thin film 11 which formed gold with the silver alloy of which 4 atom % addition was done as shown in a table 3, the very low sheet resistivity value 4.9ohm/** is shown. All were 90% or more on the wavelength whose light transmittance of each transparence multilayer electric conduction film after the annealing treatment of 1 hour is 545nm (green) at 220 degrees C. On the wavelength of 610nm (red), it is what was carried out 4 atom % addition, and 89% and light transmittance are falling gold for a while. Addition of the gold which exceeds 4 atom % also from the point of light transmittance is not not much desirable.

[0087] moreover, the place which kept each transparence multilayer electric conduction film under 60 degrees C and the high-humidity/temperature atmosphere of 95% of relative humidity, and observed appearance change 200 hours after -- any -- silverfish -- it was good without generating. Moreover, when the appearance of each transparence multilayer electric conduction film kept on these conditions for 500 hours was seen, there was no appearance change in what added gold at a rate more than 0.4 atom %. Minute silverfish had occurred in what added the gold of 0.1 atoms % and 0.2 atom %. All were better than the multilayer electric conduction film which has the silver copper alloy which added copper as a silver system thin film.

[0088] In example 7 this example, the transparent electrode plate which has the multilayer electric conduction film of this invention was produced. This transparent electrode plate has the structure shown in drawing 1 , was equipped with the transparence multilayer electric conduction film 10 which consists of a transparence oxide thin film 12 with a thickness of 39nm by which the laminating was carried out one by one on 0.7mm glass substrate SUB in thickness, and the silver thin film 11 with a thickness of 15nm and the transparence oxide thin film 13 with a thickness of 40nm, and produced it by the approach of an example 1 and resemblance.

[0089] Each formed the transparence oxide thin films 12 and 13 with the mixed oxide contained by metallic element conversion (an oxygen atom is not counted) at a rate of indium 66 atom %, cerium 32.5 atom %, tin 1.0 atom %, and titanium 0.5 atom %. Moreover, the silver system thin film 11 was formed with the silver-golden-copper ternary alloy which consists of silver 98.4 atom %, golden 0.8 atom %, and copper 0.8 atom %.

[0090] This transparence multilayer electric conduction film showed the sheet resistivity of 2.8ohms / ** after the annealing treatment of 1 hour at 220 degrees C, and the light transmittance in 550nm was about 97%. Moreover, when this transparence multilayer electric conduction film was kept for 200 hours under 60 degrees C and the high-humidity/temperature condition of 95% of relative humidity, there is no generating of silverfish and the good appearance was presented.

[0091] Thus, the multilayer electric conduction film which formed the silver system thin film with the silver-golden-copper ternary alloy is in the inclination whose moisture resistance also improves while being in the inclination which shows lower sheet resistivity compared with the multilayer electric conduction film in which the silver system thin film was formed, with the silver-golden binary alloy containing the gold of the amount equivalent to the total quantity of the gold and copper. Moreover, since gold is more expensive than silver about 100 times, it can make a golden addition low and can also reduce cost.

[0092] In example 8 this example, the transparent electrode plate which has the multilayer electric conduction film of this invention was produced. The transparence oxide thin film 12 with a thickness of 40nm by which this transparent electrode plate has the structure shown in drawing 2 , carried out location adjustment respectively on glass substrate SUB with a thickness of 0.77mm, and the laminating was carried out to the electrode configuration, It has two or more

transparence multilayer electric conduction film 10 which consists of a silver thin film 11 with a thickness of 14nm and a transparence oxide thin film 13 with a thickness of 40nm, and has the dampproof transparence thin film 21 of electric insulation with a thickness of 40nm which covers uniformly all this transparence multilayer electric conduction film 10, and protects that front face and a side edge side.
[0093] The transparence oxide thin films 12 and 13 are all metallic element conversions (an oxygen atom is not counted), and were used as the mixed oxide which added the zirconium dioxide to indium oxide at a rate that a zirconium element becomes 10 atom %. Moreover, the above-mentioned dampproof transparence thin film 21 is formed by silicon oxide (SiO2). Each transparence multilayer electric conduction film (transparent electrode) 10 has the stripe configuration which has width of face of 200 micrometers, and is formed at intervals of [ of 10 micrometers ] pitch 210micrometer.
[0094] After this transparent electrode plate formed the transparence oxide thin film 12, the silver system thin film 11, and the transparence oxide thin film 13 on Substrate SUB according to the technique of an example 1 and etched them into the stripe pattern, it formed the dampproof transparence thin film 21, and formed, then performed annealing treatment for 30 minutes at 200 degrees C. In addition, each transparent electrode was what has a detailed width-of-face part with a width of face of 20nm or less.
[0095] The sheet resistivity of the obtained transparent electrode was about 2.8ohm/**. When this transparent electrode plate was left for one month and observed in air, change of an appearance was not observed at all on the surface of the transparent electrode.
[0096] In addition, when the silver thin film was formed on the glass substrate and this was left for one month in air for the comparison, the front face discolored and much silverfish were observed. Thus, since degradation of a silver system thin film with the passage of time is prevented and the preservation stability improves, it has the effectiveness that it is stabilized and a liquid crystal display without the display defect resulting from the sulfur compound and moisture in air etc. can be manufactured.
[0097] In example 9 this example, the transparency mold liquid crystal display shown in drawing 3 was created. Transparent electrode 421 Or 42n It has a stripe configuration with a width of face of 100 micrometers, and is prepared by pitch 110micrometer, respectively. Moreover, the transparent electrode 34 had the stripe configuration with a width of face of 320 micrometers, and has extended in the direction which is pitch 330micrometer and intersects perpendicularly with the extension direction of a transparent electrode 42 on a light filter CF. In addition, each transparent electrode was what has a detailed width-of-face part with a width of face of 20nm or less.
[0098] Transparent electrodes 34 and 42 all consist of the transparence oxide thin film 12 of 38nm of thickness, a silver system thin film 11 of 14nm of thickness, and a transparence oxide thin film 13 of 41nm of thickness.
[0099] The refractive index of the transparence oxide thin films 12 and 13 is 2.2, all consist of a mixed oxide of indium oxide and cerium oxide, and the cerium of the presentation is 25 atoms % in metal atom conversion with an indium and a cerium. The silver system thin film 11 is formed with the silver-copper alloy which does 0.8 atom % content of copper.
[0100] Before these transparent electrodes' 34 and 42 being produced by the same technique as an example 1, etching them, forming them and constructing to a liquid crystal cell, annealing treatment of 1 hour was performed at 220 degrees C, and the sheet resistivity at that time was about 3ohm/**.
[0101] When the same thickness as this example compared brightness with the liquid crystal display using the transparent electrode of 3 lamination by the transparence oxide thin film of ITO (refractive index 2 [ about ]) as an example of a comparison, about 10%, this example was brighter and its display grace was high.
[0102] Furthermore, there was also no aging, and the transparent electrode of this example did not have a cross talk as compared with the transparent electrode (8ohm/**) of the conventional ITO monolayer, either, and was very high display grace also at the point of liquid crystal actuation.

[0103] an example 10 -- the light reflex nature electrode plate was produced in this example. This light reflex nature electrode plate had the structure shown in drawing 1 , and is equipped with the light reflex nature electric conduction film (electrode) 10 which consists of the transparence oxide thin film 12 with a thickness of 10nm by which the laminating was carried out one by one on glass substrate SUB with a thickness of 0.7mm, a silver system thin film 11 with a thickness of 120nm, and a transparence oxide thin film 13 with a thickness of 70nm.
[0104] The transparence oxide thin films 12 and 13 are formed by each with the thin film of the indium oxide containing a zirconium dioxide, and the content of a zirconium dioxide is metallic element conversion (an oxygen atom is not counted), and they are amounts from which a zirconium atom becomes 20 atom % to an indium atom. Moreover, the silver system thin film 11 is formed with the silver-copper alloy which does 1 atom % content of copper.
[0105] After forming and etching the transparence oxide thin film 12, the silver system thin film 11, and the transparence oxide thin film 13 according to the technique of an example 1, annealing treatment of 1 hour was performed at 220 degrees C.
[0106] In this way, the rate of a light reflex of aluminum is compared as 100% about the spectral reflectance of the obtained light reflex electric conduction film, and the result is shown in drawing 12 . The light reflex nature electric conduction film was created using the silver independent thin film which does not contain copper as the above-mentioned silver system thin film for the comparison. Although this light reflex nature electric conduction film showed the rate of a light reflex of a visible region almost higher than aluminum in the whole region, it showed about 86% of low rate of a light reflex in the visible region by the side of the short wavelength of about 450nm.
[0107] on the other hand, the light reflex nature electric conduction film of this example which used the thin film of the silver alloy which added copper is shown in drawing 12 -- also in the visible region by the side of the low wavelength of about 450nm, the rate of a light reflex higher than aluminum is shown like, and it has checked having a uniform and high rate of a light reflex in all visible regions.
[0108] The light reflex nature electric conduction film concerning this example was left for two months in air, and change of the light reflex property was inspected. Consequently, an exterior change was not observed at all on the front face of a silver system thin film, and there was also no change of the rate of a light reflex.
[0109] Except for the point which used the indium oxide thin film which contains titanium oxide as example 11 transparence oxide thin films 12 and 13, and used the silver-copper alloy thin film which contains the copper of various amounts as a silver system thin film, glass substrate production of the light reflex nature electric conduction film was carried out like the example 10. The content of the titanium oxide in the transparence oxide thin films 12 and 13 is an amount from which a titanium atom becomes 20 atom % to an indium atom.
[0110] In this way, the rate of a light reflex to the 450nm light was measured about the obtained various light reflex nature electric conduction film, respectively. This result is shown in drawing 13 . From drawing 13 , the light reflection factor by the side of the short wavelength of about 450nm is changed with the content of the above-mentioned copper. When the rate of a light reflex of aluminum is compared as 100%, at 0% of copper content About 86% of the rate of a light reflex of aluminum It has checked reaching about 102 - 104% of peak prices by the copper content 1 thru/or 3 atom % about 97% in copper content 0.1 atom %, and falling to about 97% by copper content 7 atom %.
[0111] an example 12 -- in this example, the light reflex nature electrode plate was produced like the example 10. This light reflex nature electrode plate has the structure shown in drawing 2 . On glass substrate SUB with a thickness of 0.7mm Location adjustment is carried out respectively. Two or more multilayer light reflex nature electric conduction film 10 which consists of an optical reflexibility silver system thin film 11 which consists of the transparence oxide thin film 12 with a thickness of 10nm and the silver with a thickness of 120nm by which the laminating was carried out to the electrode configuration, and a transparence oxide thin film 13 with a thickness of 70nm, and these multilayer light reflex nature electric conduction film 10 are covered uniformly. It has the dampproof transparence thin film 21 with a thickness of 35nm

which protects the front face and a side edge side.
[0112] The transparence oxide thin films 12 and 13 are all metallic element conversions (an oxygen atom is not counted), and are formed with the mixed oxide which added the zirconic acid ghost to indium oxide at a rate that a zirconium atom becomes 3 atom %. Moreover, the dampproof transparence thin film 12 is formed by silicon oxide. Each light reflex nature electrode has a stripe configuration with a width of face of 200 micrometers, and is arranged at intervals of [ of 10 micrometers ] pitch 210micrometer. In addition, each light reflex nature electrode was what has a detailed width-of-face part with a width of face of 20nm or less which is a circuit pattern for mounting of IC for liquid crystal actuation.
[0113] After this light reflex nature electrode applied correspondingly and formed the transparence oxide thin film 12, the silver system thin film 11, and the transparence oxide thin film 13 according to the technique of an example 1 and performed patterning by etching, it formed the dampproof transparence thin film 21, then performed and formed the annealing treatment for 30 minutes at 220 degrees C.
[0114] In this way, the obtained light reflex nature electrode plate was left for one month in air, and change of the light reflex property was inspected. Consequently, change of an appearance was not observed at all on the front face of the optical reflexibility silver thin film 11, and there was also no change of the rate of a light reflex.
[0115] an example 13 -- in this example, the reflective mold liquid crystal display of the structure shown in drawing 4 was produced. It sets to this liquid crystal display, and is a transparent electrode 531. Or 53n It has a stripe configuration with a width of face of 100 micrometers, and is arranged by pitch 110micrometer on the light-scattering film 52, respectively. Moreover, each light reflex nature electrode 62 has a stripe configuration with a width of face of 320 micrometers, and it is pitch 330micrometer, and it intersects perpendicularly with the extension direction of a transparent electrode 53, and it is carrying out direction extension. In addition, the transparent electrode 53 and the light reflex nature electrode 62 were what has a detailed width-of-face part with a width of face of 20nm or less, respectively.
[0116] A transparent electrode 53 consists of the transparence oxide thin film 12 of 40nm of thickness, a silver system thin film 11 of 15nm of thickness, and a transparence oxide thin film 13 of 40nm of thickness. The light reflex nature electrode 62 consists of the transparence oxide thin film 12 of 10nm of thickness and the silver system thin film 11 of 150nm of thickness which touch the tooth-back substrate 61 which is a glass substrate, and a transparence oxide thin film 13 of 40nm of thickness.
[0117] Also in any of a transparent electrode 53 and the light reflex nature electrode 62, the transparence oxide thin films 12 and 13 30 atom % Were mixed oxides with the included indium oxide in metallic element conversion about cerium oxide, and the refractive index was 2.24. Also in any of a transparent electrode 53 and the light reflex nature electrode 62, the silver system thin film 11 was formed with the silver-copper alloy which does 0.8 atom % content of copper.
[0118] As an example of a comparison, electrodes 53 and 62 were formed by sheet resistivity 8ohm/**, and ITO of 240nm of thickness, and the same liquid crystal display as this example was produced at the rear face (outside) of the tooth-back substrate 61 except reflecting plate ****** of aluminum. When the brightness of the liquid crystal display of this example and the example of a comparison was compared, this example was brighter about 10%, and display quality was high. Moreover, although shadowing was observed by the graphic character in the display of the example of a comparison, shadowing was not observed at all in the display of this example. Moreover, although the graphic character was reflected in the aluminum reflecting plate and the alphabetic character was visible to the duplex in the display of the example of a comparison, such a phenomenon was not produced in the display of this example.
[0119]
[Effect of the Invention] As stated above, according to this invention, a thin film shows good conductivity and the electric conduction film degradation with the passage of time moreover excelled [ film ] in preservation stability few is offered. This electric conduction film is useful also not only as the transparent electrode and transparent electrode of a liquid crystal display but a light reflex nature electrode.

[Translation done.]

* NOTICES *



## DESCRIPTION OF DRAWINGS

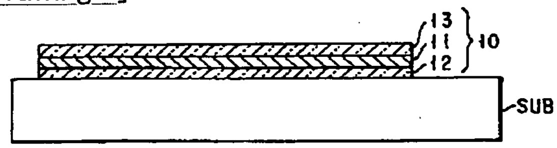
[Brief Description of the Drawings]
[Drawing 1] The sectional view of the multilayer electric conduction film of this invention formed on the substrate.
[Drawing 2] The sectional view of the multilayer electric conduction film of this invention of a gestalt protected by the protective coat.
[Drawing 3] The sectional view showing roughly the transparency mold liquid crystal display with which the multilayer electric conduction film of this invention may be applied.
[Drawing 4] The sectional view showing roughly the reflective mold liquid crystal display with which the multilayer electric conduction film of this invention may be applied.
[Drawing 5] The graphical representation showing the relation between the thickness of the silver system thin film in the multilayer electric conduction film of this invention, the light transmittance of the multilayer electric conduction film concerned, and the rate of a light reflex.
[Drawing 6] Another graphical representation showing the relation between the thickness of the silver system thin film in the multilayer electric conduction film of this invention, the light transmittance of the multilayer electric conduction film concerned, and the rate of a light reflex.
[Drawing 7] Another graphical representation to the pan in which the relation between the thickness of the silver system thin film in the multilayer electric conduction film of this invention, the permeability of the multilayer electric conduction film concerned, and a reflection factor is shown.
[Drawing 8] The graphical representation showing the relation of the copper amount and the light transmittance of the multilayer electric conduction film which were added by the silver system thin film.
[Drawing 9] The graphical representation showing the relation of the copper amount and the sheet resistivity of the multilayer electric conduction film which were added by the silver system thin film.
[Drawing 10] The graphical representation showing the relation between the refractive index of a transparence oxide thin film, the light transmittance of the multilayer electric conduction film, and the rate of a light reflex.
[Drawing 11] The graphical representation showing the light transmittance of the multilayer electric conduction film manufactured in the example of this invention.
[Drawing 12] The graphical representation showing the light transmittance of the multilayer electric conduction film manufactured in other examples of this invention.
[Drawing 13] The graphical representation showing the relation of the copper amount and the rate of a light reflex which were added by the base electric conduction film of the multilayer electric conduction film manufactured in the example of further others of this invention.
[Description of Notations]
11 -- Silver system thin film
12 13 -- Transparence oxide thin film
21 -- Dampproof transparence thin film
31, 41, 51, 61, SUB -- Substrate
34,421-42n and 531-53n -- Transparent electrode

36, 44, 55 -- Polarization film
52 56 -- Light-scattering film
62 -- Light reflex nature electrode
CF1 -CFn -- Light filter
LC -- Liquid crystal ingredient

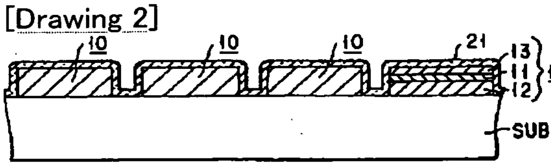
[Translation done.]

DRAWINGS

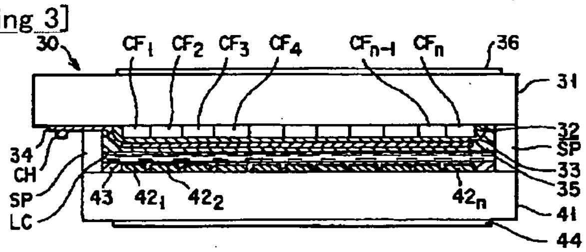
[Drawing 1]



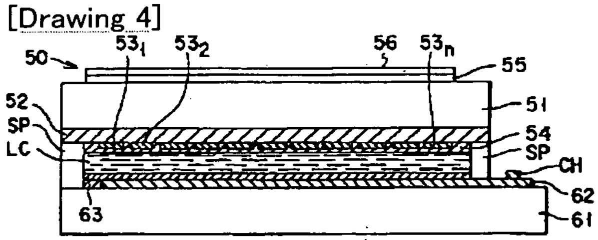

[Drawing 2]



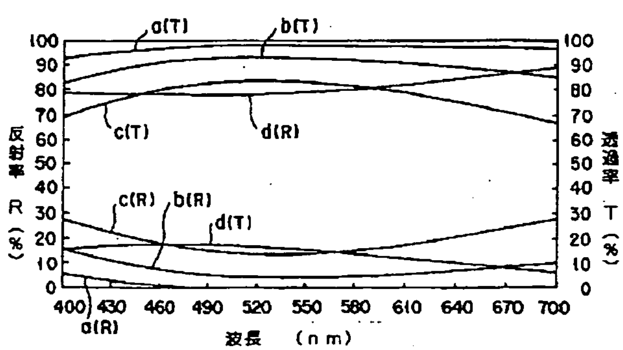

[Drawing 3]



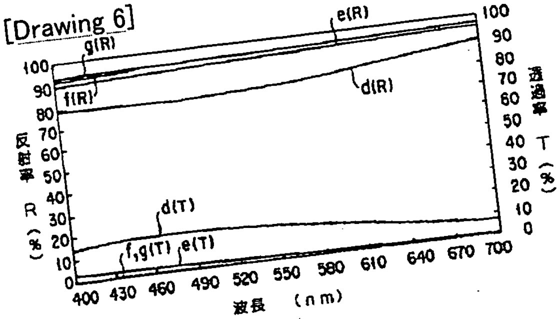

[Drawing 4]



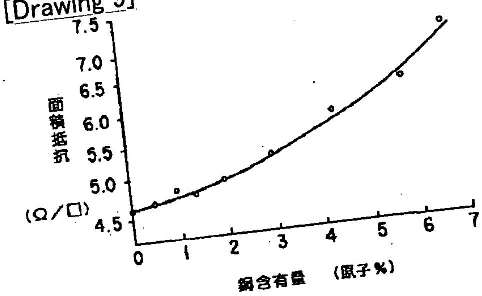

[Drawing 5]



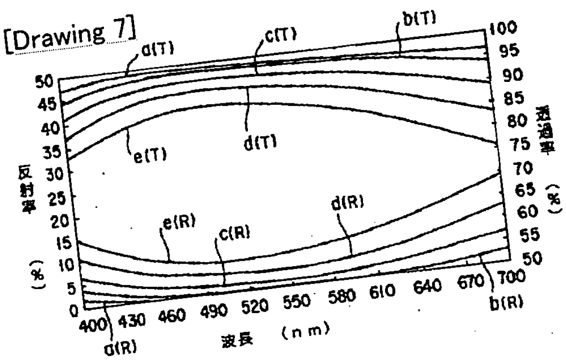
[Drawing 6]



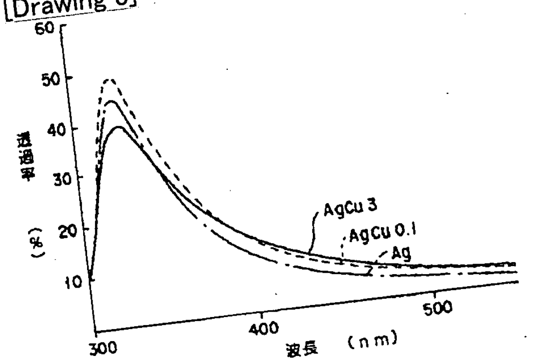

[Drawing 9]



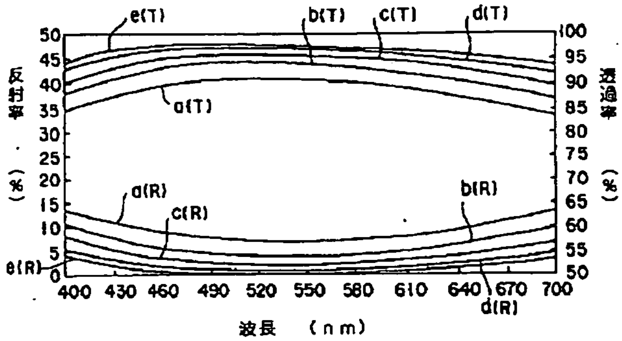

[Drawing 7]



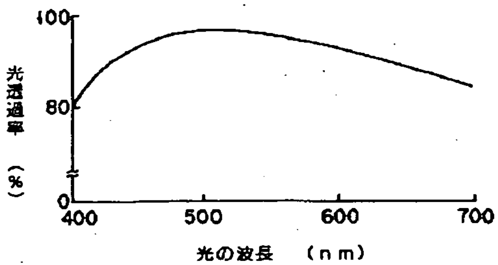

[Drawing 8]



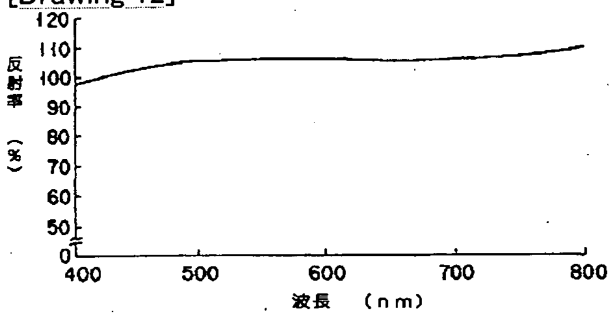

[Drawing 10]



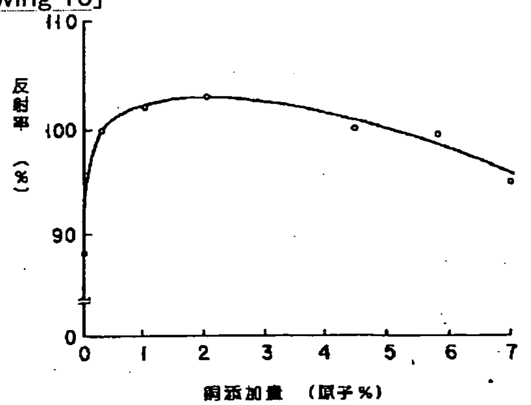

[Drawing 11]




[Drawing 12]




[Drawing 13]




[Translation done.]